Phosphinite-Ni(0) Mediated Formation of a Phosphide-Ni(II)-OCOOMe Species via Uncommon Metal−Ligand Cooperation

Yeong-Eun Kim, Seohee Oh, Seji Kim, Onnuri Kim, Jin Kim, Sang Woo Han, and Yunho Lee*

Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

S *Supporting Information*

ABSTRACT: Reversible transformations are observed between a phosphide-nickel(II) alkoxide and a phosphinite-nickel(0) species via a P−O bond formation coupled with a 2-e⁻ redox change at the nickel center. In the forward reaction, the nickel(0) dinitrogen species $(PP^{OMe}P)Ni(N_2)$ (**2**) and $\{(PP^{OMe}P)Ni\}_2(\mu\text{-}N_2)$ (**3**) were formed from the reaction of (PPP)NiCl (**1**) with a methoxy anion. In the backward reaction, a (PPP)Ni(II) moiety was regenerated from the CO_2 reaction of **3** with the concomitant formation of a methyl carbonate ligand in (PPP)Ni(OCOOMe) (**7**). Thus, unanticipated metal−ligand cooperation involving a phosphide based ligand is reported.

Metal−ligand cooperation is recently emphasized as a unique synthetic methodology to expand the role of transition metal ions in multielectron catalytic reactions.[1] As a classical example, an $Fe^{IV}(O)$ species supported by a cationic porphyrin π-radical has been known as the key intermediate in cytochrome P450.[2] Various ligand types such as salicylaldimine (salen) equipped with phenolate groups, catecholate, and phenylenediamine along with their derivatives were reported as redox-active ligands.[1,3] Chirik and co-workers reported a series of iron and cobalt complexes supported by aryl-substituted bis(imino)pyridine ligands.[4] Redox and chemically active ligands assist transition metals to achieve catalysis for various bond-forming reactions.[4] More recently, metal−ligand cooperativity mediated by aromatization/dearomatization is utilized as a versatile methodology when working with group 10 transition elements. Various catalytic reactions employing pincer type ligands based on pyridine, acridine, and phenanthroline scaffolds were demonstrated by Milstein and co-workers.[5] In most of the exemplified noninnocent ligands, a π-conjugated system is employed in which the reasonable ligand activity can be coupled with the metal's redox change. While various phosphine ligands have been widely utilized in organometallic chemistry, examples of a "noninnocent" phosphine ligand are relatively rare. Recently, Thomas and co-workers reported a new type of pincer ligand containing a central cationic N-heterocyclic phosphenium (NHP) donor.[6] Its transition metal complexes of Pt, Pd, Cu, and Co reveal the noninnocent behavior of an NHP unit with interconversion of NHP^+ and NHP^-. Radosevich and co-workers reported reversible P^{III}/P^V redox cycling utilized for catalytic transfer hydrogenation, along with E−H oxidative addition (E = O, N) in a compound containing a three-coordinate phosphorus center.[7] In fact, Gabbaï and co-workers reported a Ni/Sb

platform in which the antimony ligand as a redox active ligand can be switched from an L to X to Z type ligand by successive formal one-electron redox processes.[8] With this in mind, we have worked with an anionic PPP ligand $(PPP^- = P[2\text{-}P^iPr_2\text{-}C_6H_4]_2^-)$ previously reported in the literature[9] in which a central anionic phosphide moiety can be functionalized/defunctionalized with an alkoxy group via the reversible formation of a phosphinite moiety, *vide infra*. Our strategy is to couple the reversible phosphide/phosphinite interconversion of a PPP ligand with a redox change that allows the central metal to go from a square planar nickel(II) to tetrahedral nickel(0) with a π-acidic ligand (Scheme 1). This chemistry is reminiscent of the

Scheme 1
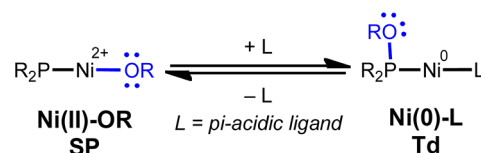
previous example with a PNP pincer ligand $(N[2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3]_2^-)$ in which oxidative addition of N−C and N−H bonds occur at a low valent metal center, as reported by Ozerov and co-workers.[10]

Herein, we report an uncommon transformation involving a stable zerovalent nickel dinitrogen species, $\{(PP^{OMe}P)Ni\}_2(\mu\text{-}N_2)$ (**3**), obtained from the reaction of (PPP)NiCl (**1**) with a methoxy anion via a P−O bond formation, coupled with a two-electron reduction on nickel. In the reverse reaction, a nickel(II)-methyl carbonate species, (PPP)Ni(OCOOMe) (**7**), was successfully produced from the reaction of **3** with CO_2, revealing methoxy group transfer from a phosphinite moiety to a bound CO_2 ligand. This is a rare case where metal redox activity is tightly coupled with a two-electron group transfer reaction via metal−ligand cooperation within a phosphine−metal complex system.

Unanticipated production of a nickel(0) dinitrogen species was accomplished by the addition of 1 equiv of NMe_4OH to a red purple solution of (PPP)NiCl (**1**) in THF/MeOH under N_2 (Scheme 2). The resulting diamagnetic product was isolated as a dark brown solid (83%); its C_6D_6 solution reveals the presence of two nickel dinitrogen species $(PP^{OMe}P)Ni(N_2)$ (**2**) and $\{(PP^{OMe}P)Ni\}_2(\mu\text{-}N_2)$ (**3**) detected as a mixture in the NMR spectrum. When the same NMR sample was exposed to vacuum, a set including a triplet at 132.37 ppm ($J_{PP} = 98.8$ Hz) and a

Scheme 2
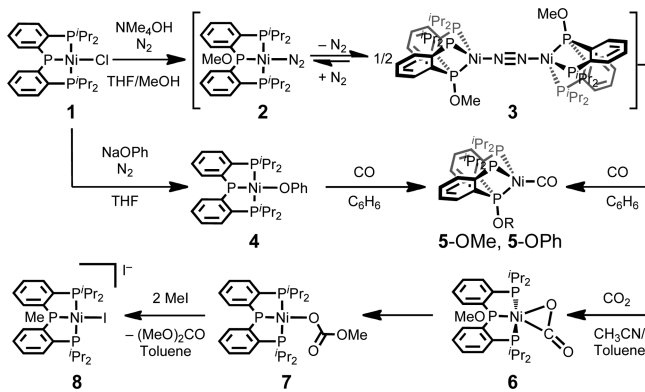
doublet at 60.60 ppm (J_{PP} = 98.8 Hz) assigned to **3** was found to have grown in ^{31}P NMR spectrum. Another set that includes a triplet at 139.34 ppm (J_{PP} = 82.7 Hz) and a doublet at 61.55 ppm (J_{PP} = 83.6 Hz) was singly observed when a lower concentration (0.54 mM) of **2** was present (Supporting Information). A similar solution behavior of mono- and dinuclear species in equilibrium was previously observed for an analogous nickel(0) dinitrogen species {(PP^{Me}P)Ni}$_2$(μ-N$_2$).[11]

The solid state structure of **3** confirms a dinuclear nickel end-on bridging N$_2$ adduct (Figure 1a). Its N−N distance of 1.112(5)
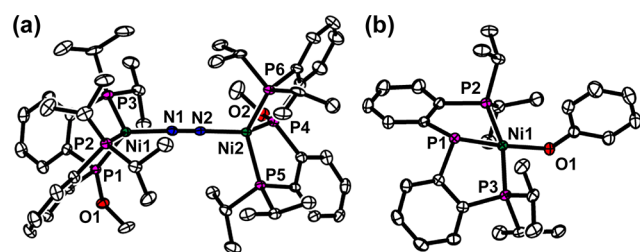

Figure 1. Displacement ellipsoid (50%) representation of (a) {(PP^{OMe}P)Ni}$_2$(μ-N$_2$) (**3**) and (b) (PPP)Ni(OPh) (**4**). Hydrogen atoms and molecules of cocrystallization are omitted for clarity.

Å (Table 1) supports a triple bond character indicating weak nickel-based π-back bonding. The bridging N$_2$ ligand of **3** was also confirmed by a N$_2$ Raman vibration at 2038 cm^{-1} ($\Delta(^{15}$N$_2$) = −64 cm^{-1}), similar to previously reported Ni(0)−μ-N$_2$−Ni(0) species.[11] In the solution IR spectrum of **2**, a peak at 2094 cm^{-1} ($\Delta(^{15}$N$_2$) = −70 cm^{-1}) was assigned to the vibration of the terminal dinitrogen ligand (Supporting Information). The apparent weak binding of N$_2$ in both **2** and **3** suggests an equilibrium under 1 atm of N$_2$(g) at room temperature with the estimated equilibrium constant as 34.0 ± 9.2 in favor of **3** in C$_6$D$_6$

as measured by the ^{1}H NMR signals at ∼3.5 ppm (Scheme 2). This equilibrium was also confirmed by ^{15}N NMR spectroscopy experiments (−50.0 and −71.7 ppm for **2** and −72.2 ppm for **3** at −60 °C in toluene-d_8; see Supporting Information). The structural and spectroscopic data of **3** unambiguously reveal the presence of a phosphinite moiety (P1 and P4 in Figure 1a). In order to confirm the origin of a methoxy group, CD$_3$OD was used to synthesize {(PP^{OCD3}P)Ni}$_2$(μ-N$_2$) (**3-OCD$_3$**) under the same conditions. Both ^{31}P and ^{1}H NMR data suggest that the identical species was obtained except for the absence of the signal corresponding to a methoxy group at 3.69 ppm in the ^{1}H NMR spectrum. A deuterated **3-OCD$_3$** species was also identified by cold spray ionization mass spectrometry (Supporting Information).

Conversion of (PPP)NiCl (**1**) to the corresponding zerovalent nickel dinitrogen adducts (**2** and **3**) might occur via ligand substitution at a divalent nickel center, resulting in the formation of (PPP)Ni(OMe) followed by the reductive elimination of a POMe moiety from a zerovalent nickel ion. After the rebinding of a phosphinite group, the resulting Ni(0) product is presumably further stabilized by a N$_2$ ligand. This scenario can be supported by the similar reductive elimination behavior involved in the generation of the nickel(0) dicarbonyl species with PNP pincer ligands (N(o-C$_6$H$_4$PR$_2$)$_2^-$ or N[2-PR$_2$-4-Me-C$_6$H$_3$]$_2^-$; R = Ph or ^{i}Pr) from the reaction of corresponding nickel(II) species with excess CO(g).[12] Involvement of the direct addition of methoxide onto a phosphide moiety cannot be ruled out.[6d,13]

Under a N$_2$ atmosphere, the corresponding hypothesized (PPP)Ni(OMe) could not be isolated due to the fast conversion rate of the reaction at room temperature. However, under an Ar atmosphere, an unknown species revealing a triplet at 91.32 ppm (J_{PP} = 8.3 Hz) and a doublet at 46.46 ppm (J_{PP} = 8.1 Hz) in the ^{31}P NMR spectrum was generated with other impurities from the same reaction. This spectrum is clearly different from that of zerovalent nickel species, but fairly similar to that of (PPP)Ni-(OPh) (**4**; 99.22 ppm (t, J_{PP} = 8.0 Hz), 48.61 ppm (d, J_{PP} = 8.4 Hz)), vide infra. The intermediate species slowly disappeared under the Ar atmosphere but was directly converted to **2** and **3** upon exposure to N$_2$(g) indicating the presence of (PPP)Ni-(OMe) (Supporting Information).

To attain further mechanistic insight into the formation of a nickel(0) adduct, we sought to tune the stability/reactivity of the corresponding nickel(II) alkoxide species. In the first instance, phenoxide was utilized, in which less electron density can be donated compared to alkoxides. The addition of NaOPh to the solution of **1** produces (PPP)Ni(OPh) (**4**) in high yield (90%, Scheme 2). Interestingly, the formation of the corresponding nickel(0) dinitrogen species is not detected under the same

Table 1. Selected Bond Distances and Angles of 3, 4, 5-OPh, 5-OMe, and 7

	Ni−P(1) (Å)	Ni−P(2, 3) (Å)	Ni−L^a (Å)	L−X^b (Å)	P(1)−Ni−L (deg)	P(2)−Ni−P(3) (deg)
{(PP^{OMe}P)Ni}$_2$(N$_2$) (**3**)	2.098(1)	2.161(1), 2.171(1)	1.837(4)	1.112(5)	125.4(1)	128.54(5)
	2.107(1)^c	2.173(1), 2.152(1)^d	1.839(4)^e		126.4(1)^f	131.91(5)^g
(PPP)NiOPh (**4**)	2.1506(5)	2.1995(5), 2.1805(5)	1.922(1)	1.321(2)	169.40(4)	162.43(2)
	2.1494(5)^c	2.2048(5), 2.1855(5)^d	1.946(1)^e	1.316(2)	171.53(4)^f	156.26(2)^g
(PP^{OPh}P)NiCO (**5-OPh**)	2.1231(9)	2.1868(9), 2.1894(9)	1.746(4)	1.163(4)	127.5(1)	123.64(4)
(PP^{OMe}P)NiCO (**5-OMe**)	2.1332(5)	2.1850(5), 2.1885(4)	1.747(2)	1.153(2)	128.81(5)	121.56(2)
(PPP)NiOCOOMe (**7**)	2.151(1)	2.180(1), 2.197(1)	1.940(3)	1.273(5)	170.4(1)	162.71(5)

^{a}L = N for **3**, O for **4** and **7**, C for **5-OMe** and **5-OPh**. ^{b}X = N for **3**, C for **4** and **7**, O for **5-OMe** and **5-OPh**. ^{c}Distance for Ni(2)−P(4). ^{d}Distance for Ni(2)−P(5), Ni(2)−P(6). ^{e}Distance for Ni(2)−N(2). ^{f}Angle for P(4)−Ni(2)−N(2). ^{g}Angle for P(5)−Ni(2)−P(6).

conditions; it is currently not clear why this is the case. However, the generation of a zerovalent nickel species (PP^{OPh}P)Ni(CO) (**5-OPh**) was accomplished by the addition of carbon monoxide, presumably via the similar reaction pathway described above (Scheme 2 and Figure 1b). Instantaneously, **5-OPh** was formed upon addition of CO(g) at room temperature in C_6D_6 as monitored by ^{31}P NMR spectroscopy (Supporting Information).[14] Similarly a corresponding nickel monocarbonyl species (PP^{OMe}P)Ni(CO) (**5-OMe**) was also produced by the addition of CO(g) to the C_6H_6 solution of **3**. Both nickel(0) carbonyl species were characterized by various spectroscopic techniques including X-ray crystallography. Similar ^{31}P NMR spectral signals to those of the central phosphorus atom in **5-OPh** and **5-OMe** were found to be positively shifted to 152.94 ppm (t, J_{PP} = 72.1 Hz) and 162.40 ppm (t, J_{PP} = 58.8 Hz), respectively, from that of (PPP)NiCl (**1**, 114.80 ppm) and **4** (99.22 ppm) suggesting the presence of an electron-deficient central P atom. The vibration at 1928 cm^{-1} is assigned to **5-OPh** and supports coordination of a single carbon monoxide ligand at a nickel(0) center. In the case of **5-OMe**, a carbonyl vibration appears at 1909 cm^{-1}, due to enhanced back-donation from the electron-rich Ni(0) center. Both solid structures of **5-OPh** and **5-OMe** clearly reveal a phosphinite coordination at the pseudotetrahedral nickel(0) centers (τ_4 = 0.78 and 0.77, respectively)[15] where P–O bond lengths of 1.676(2) and 1.645(1) Å were determined, respectively (Figure 2). DFT analysis on both **5-OPh** and **5-**
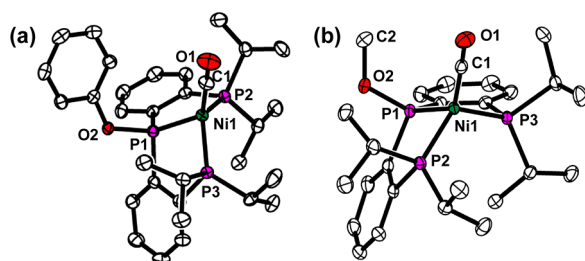

Figure 2. Displacement ellipsoid (50%) representation of (a) (PP^{OPh}P)Ni(CO) (**5-OPh**) and (b) (PP^{OMe}P)Ni(CO) (**5-OMe**). Hydrogen atoms and molecules of cocrystallization are omitted for clarity.

OMe reveal that five highest filled orbitals have significant nickel d-orbital character supporting the zerovalent nickel ion (Supporting Information).[16]

To explore the oxidative migratory methoxy group transfer of {(PP^{OMe}P)Ni}$_2$(μ-N$_2$) (**3**) with small molecule chemistry, we investigated carbon dioxide conversion. The addition of CO_2 to the CH_3CN/toluene solution of **3** results in the formation of a new divalent nickel complex (PPP)Ni(OCOOMe) (**7**) with excellent conversion (>99%, Scheme 2 and Figure 3). The ^{31}P NMR data of the product reveal a new set of signals at 99.46 (t, J_{PP} = 9.0 Hz) and 51.02 (d, J_{PP} = 8.6 Hz) ppm; these are shifted by 30 ppm from that observed for the central phosphorus atom of **3**. From a ^{13}C-labeling experiment, the ^{13}C enriched carbon dioxide moiety in **7-^{13}CO$_2$** was detected by both ^{13}C (158.10 ppm, s) and ^{1}H (3.82 ppm, d, $^3J_{CH}$ = 3.6 Hz) NMR spectroscopy. According to the IR data, a new carbonyl vibration was displayed at 1693 cm^{-1} (Δ(^{13}CO$_2$) = −56 cm^{-1}); thus the formation of a methyl carbonate moiety at the nickel center was ensured. In the CO_2(g) addition, the nickel-CO_2 adduct, (PP^{OMe}P)Ni(η^2-CO$_2$) (**6**) might be formed as a reaction intermediate, revealing an independent set of signals at 169.95 (t, J_{PP} = 9.6 Hz) and 56.47
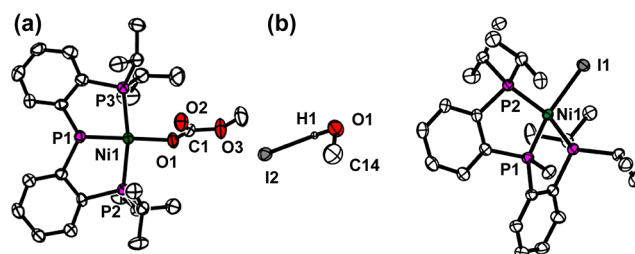

Figure 3. Displacement ellipsoid (50%) representation of (a) (PPP)Ni(OCOOMe) (**7**) and (b) {(PP^{Me}P)Ni(I)}{I·MeOH} (**8**). Hydrogen atoms and molecules of cocrystallization are omitted for clarity.

(d, J_{PP} = 9.9 Hz) ppm in ^{31}P NMR spectroscopy in C_6D_6. In addition, the ^{1}H NMR spectrum reveals a signal at 3.43 ppm (d, J_{PH} = 14.2 Hz) in support of this species possessing a P–OMe moiety (Supporting Information). This intermediate is reminiscent to the analogous species (PP^{Me}P)Ni(η^2-CO$_2$) reported by our group.[11] However, this compound is not stable in CH_3CN/toluene at room temperature; consequently it was converted to **7** and the CO_2 conversion reaction was completed within 5 h.

The X-ray structure of **7** reveals the CO_2 incorporation as the form of carbonate with a methoxy group migrated from phosphinite (Figure 3). A methyl carbonato ligand is coordinated to the nickel(II) center in which the Ni–O bond distance is 1.940(3) Å and two C–O bonds are 1.273(5) and 1.378(4) Å, with the C=O bond being 1.208(5) Å. A structurally characterized nickel(II) methyl carbonato complex supported by a tetraazacycloalkane ligand was reported by Ito and coworkers.[17]

Other structurally characterized transition metal methyl carbonato species were reported as well.[18] In particular, several metal–carbonato species were generated from the reaction of a corresponding methoxide species with carbon dioxide.[17,18b,19] However, there is no report revealing the metal methyl carbonato generation from such a phosphinito methoxide group.[20] A stoichiometric amount of methyl iodide was added to **7** resulting in the formation of dimethyl carbonate (DMC) as detected by ^{1}H NMR spectroscopy.[21] According to our initial experiments, the first methylation occurs at a central phosphide, not on the carbonato ligand; the second addition of MeI results in the formation of {(PP^{Me}P)Ni(I)}{I·MeOH} (**8**, Figure 3) with DMC (Supporting Information).

Herein, we report an unusual metal–ligand cooperation employing a (PPP)Ni scaffold in which methoxy group transfer occurs between a phosphide moiety of the ligand and the nickel ion. This cooperation involves a two-electron Ni(0/II) redox process, coupled with reversible P–O bond formation. The electron-rich Ni-phosphide can react with alkoxide to produce the phosphinite-nickel(0) dinitrogen species (**2** and **3**). The formation of (PPP)Ni(OCOOMe) (**7**) from the reaction of **3** with CO_2 reveals the regeneration of a divalent nickel center and corresponding methyl carbonate formation via migratory methoxy group transfer. Therefore, the (PPP)Ni scaffold shows that the central phosphido P reveals phosphido-phosphinite interconversion involving reversible P–O bond formation coupled with anion metathesis at a nickel center.

ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and CIF files giving characterization data for **2**–**7**, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*yunholee@kaist.ac.kr

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) (a) Luca, O. R.; Crabtree, R. H. *Chem. Soc. Rev.* **2013**, *42*, 1440–1459. (b) Praneeth, V. K. K.; Ringenberg, M. R.; Ward, T. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 10228–10234. (c) Ketterer, N. A.; Fan, H.; Blackmore, K. J.; Yang, X.; Ziller, J. W.; Baik, M.-H.; Heyduk, A. F. *J. Am. Chem. Soc.* **2008**, *130*, 4364–4374. (d) Chaudhuri, P.; Verani, C. N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Weighardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 2213–2223. (e) See also Forum Articles on Redox-Active Ligands: *Inorg. Chem.* **2011**, *50*, 9737–9914.

(2) (a) Rittle, J.; Green, M. T. *Science* **2010**, *330*, 933–937. (b) Poulos, T. L. *Chem. Rev.* **2014**, *114*, 3919–3962.

(3) Lyons, C. T.; Stack, T. D. P. *Coord. Chem. Rev.* **2013**, *257*, 528–540.

(4) (a) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794–13807. (b) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340–13341. (c) Sylvester, K. T.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 8772–8774. (d) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. *Science* **2012**, *335*, 567–570. (e) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745–1776.

(5) (a) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588–602. (b) Langer, R.; Fuchs, I.; Vogt, M.; Balaraman, E.; Diskin-Posner, Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Chem.—Eur. J.* **2013**, *19*, 3407–3414. (c) Vogt, M.; Nerush, A.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. *Chem. Sci.* **2014**, *5*, 2043–2051.

(6) (a) Day, G. S.; Pan, B.; Kellenberger, D. L.; Foxman, B. M.; Thomas, C. M. *Chem. Commun.* **2011**, *47*, 3634–3636. (b) Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Organometallics* **2011**, *30*, 5560–5563. (c) Pan, B.; Xu, Z.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Inorg. Chem.* **2012**, *51*, 4170–4179. (d) Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Dalton Trans.* **2012**, *41*, 9083–9090. (e) Knight, S. E.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. *Inorg. Chim. Acta* **2014**, *422*, 181–187.

(7) (a) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134*, 11330–11333. (b) McCarthy, S. M.; Lin, Y.-C.; Devarajan, D.; Chang, J. W.; Yennawar, H. P.; Rioux, R. M.; Ess, D. H.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136*, 4640–4650. (c) Zhao, W.; McCarthy, S. M.; Lai, T. Y.; Yennawar, H. P.; Radosevich, A. T. *J. Am. Chem. Soc.* **2014**, *136*, 17634–17644.

(8) Jones, J. S.; Wade, C. R.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2014**, *53*, 8876–8879.

(9) Mankad, N. P.; Rivard, E.; Harkins, S. B.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 16032–16033.

(10) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792–4793.

(11) Kim, Y.-E.; Kim, J.; Lee, Y. *Chem. Commun.* **2014**, *50*, 11458–11461.

(12) (a) Yoo, C.; Kim, J.; Lee, Y. *Organometallics* **2013**, *32*, 7195–7203. (b) Liang, L.-C.; Hung, Y.-T.; Huang, Y.-L.; Chien, P.-S.; Lee, P.-Y.; Chen, W.-C. *Organometallics* **2012**, *31*, 700–708.

(13) (a) Esteruelas, M. A.; López, A. M.; Tolosa, J. I.; Vela, N. *Organometallics* **2000**, *19*, 4650–4652. (b) Jörg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92–93. (c) Weinand, R.; Werner, H. *Chem. Ber.* **1986**, *119*, 2055–2058.

(14) It is not clear that the migration of a PhO group occurs before or after CO binding.

(15) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.

(16) According to DFT analysis on (PPP)NiCl (**1**) and (PPP)NiOPh (**4**), significant nickel d-orbital character can be found in HOMOs, while $d_{x^2-y^2}$ character was found in the LUMO, suggesting that both complexes possess a d^8 Ni(II) center. In fact, the HOMO for **1** and HOMO–1 for **4** possess the significant contribution of a central phosphorus atom indicating the presence of a Ni(II)-bound electron-rich phosphide moiety in both species; see Supporting Information. In addition, the nickel's oxidation state and the electronic nature of the central phosphorus atom in **1**–**5** and **7** can be evaluated by comparing their ^{31}P NMR and XRD data; see Table S7.

(17) Kato, M.; Ito, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 285–294.

(18) (a) Peter, A.; Vahrenkamp, H. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2347–2351. (b) Brombacher, H.; Vahrenkamp, H. *Inorg. Chem.* **2004**, *43*, 6042–6049. (c) Yan, Y.-K.; Koh, W.; Jiang, C.; Leong, W. K.; Hor, T. S. A. *Polyhedron* **2000**, *19*, 641–647. (d) Ruf, M.; Vahrenkamp, H. *Inorg. Chem.* **1996**, *35*, 6571–6578. (e) Mandal, S. K.; Ho, D. M.; Orchin, M. *Organometallics* **1993**, *12*, 1714–1719. (f) Ishida, T.; Hayashi, T.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1992**, *31*, 4481–4485. (g) Kato, M.; Ito, T. *Inorg. Chem.* **1985**, *24*, 509–514. (h) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35–L36.

(19) (a) Truscott, B. J.; Nelson, D. J.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2014**, *50*, 286–288. (b) Arunachalampillai, A.; Loganathan, N.; Wendt, O. F. *Polyhedron* **2012**, *32*, 24–29. (c) Ibrahim, M. M.; Ichikawa, K.; Shiro, M. *Inorg. Chem. Commun.* **2003**, *6*, 1030–1034. (d) Aresta, M.; Dibenedetto, A.; Pastore, C. *Inorg. Chem.* **2003**, *42*, 3256–3261.

(20) There are several examples revealing alkoxide elimination from the metal-phosphinite species. (a) Nakazawa, H.; Miyoshi, Y.; Katayama, T.; Mizuta, T.; Miyoshi, K.; Tsuchida, N.; Ono, A.; Takano, K. *Organometallics* **2006**, *25*, 5913–5921. (b) Nakazawa, H.; Yamaguchi, Y.; Mizuta, T.; Miyoshi, K. *Organometallics* **1995**, *14*, 4173–4182.

(21) Product DMC (~10%) generated from the reaction was detected by ^{1}H NMR spectroscopy in toluene with internal standard 1,1,2,2-tetrachloroethane by comparison with an authentic sample of DMC; see Supporting Information.